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Recent developments on heterogeneous catalysts for biodiesel production by oil esterification and transesterification reactions: A review

M.E. Borges*, L. Díaz

Chemical Engineering Department, University of La Laguna, Avda. Astrofísico Fco. Sánchez s/n, La Laguna, Tenerife, Canary Island, 38200, Spain

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ABSTRACT

Heterogeneous catalysis is widely applied in industry due to important advantages it offers to chemical processes such as improved selectivity and easy catalyst separation from reaction mixture, reducing process stages and wastes. This is the reason why nowadays heterogeneous catalysts are being developed to produce biodiesel. Several catalytic materials have been showed in bibliography: acid solids capable to carry out free fatty acids esterification reaction, base solids which are able to carry out triglycerides transesterification reaction and bifunctional solids (acid–base character) which show ability to simultaneously catalyze esterification and transesterification reaction. This review discusses the latest advances in research and development related with heterogeneous catalysts used to produce biodiesel.

Contents

1. Introduction

Nowadays, the world's total energy output is mainly generated from fossil fuels and experts have warned about the depletion of this actual source in the near future. Besides, the increasing environmental impact care has imposed restrictions on fuel combustion emissions. These facts have stimulated the alternative sources for fossil fuel development. One of the most promising sources is biodiesel, an alternative diesel fuel derivate from renewable sources with high quality, which allows the substitution of fossil diesel oil without engine modifications [1,2]. Biodiesel shows a favorable combustion emission profile, producing much less carbon monoxide, sulfur dioxide and unburned hydrocarbons than petroleum-based diesel fuel [3,4].

Biodiesel can be chemically defined as a fuel composed of mono-alkyl esters of long chain fatty acids derived from renewable sources, such as vegetable oils and animal fats [5]. Several vegetable oils varieties such as canola, palm, palm kernel, sunflower and coconut oil have been studied as feedstocks for biodiesel production. The main disadvantage concerning about biodiesel production from these feedstocks is the high price of combustible vegetable oils compared to that of fossil based diesel fuel. As a result, non-edible oils such as Jatropha or waste cooking oils are preferred for biodiesel production due to their low price [6]. New generation biodiesel intends to derive raw material from algae and other renewable feedstock which will provide sustainability to the whole biodiesel production process needed to adequately justify the biodiesel industry [7].

For commercial fuel use, the finished biodiesel must be analyzed using sophisticated analytical equipment to ensure it meets international standards. A few specifications have been set but the ASTM D 6751 and EN 14214 standards are the most commonly used standards [2].

There are several methods for biodiesel production and application: direct use of vegetable oil, microemulsions, thermal cracking (pyrolysis) and transesterification [8]. Direct use of vegetable oil is not applicable to most of actual diesel engines, as the high viscosity would damage the engine. Biodiesel obtained from microemulsion and thermal cracking methods would lead to incomplete combustion due to a low cetane number. Transesterification is the most

* Corresponding author.
E-mail address: eborges@ull.es (M.E. Borges).

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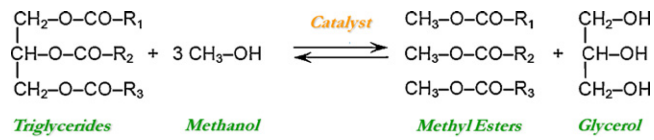


Fig. 1. Triglycerides transesterification reaction with methanol.

common method for biodiesel production due to its simplicity and it has been widely studied and industrially used to convert vegetable oil into biodiesel [9].

Transesterification is the reaction process by means of which triglyceride molecules present in animal fats or vegetable oils react with an alcohol in the presence of a catalyst to form esters and glycerol (Fig. 1). When the transesterification reaction with alcohol proceeds, the first step is the triglycerides to diglycerides conversion, which is followed by the subsequent higher glycerides to lower glycerides conversion and then to glycerol, yielding one methyl ester molecule from each glyceride at each step (Fig. 2) [10,11].

Different types of alcohols such as methanol, ethanol, propanol and butanol can be used in order to produce biodiesel. However, methanol and ethanol are the most widely used. When methanol is used as reactant, reaction product will be a fatty acid methyl esters mixture (FAME), whereas if ethanol is used as reactant, a fatty acid ethyl esters mixture (FAEE) will be obtained. Nevertheless, methanol is commonly used in biodiesel production due to its low cost and industrial availability [12].

The catalyst presence is necessary to increase the reaction rate and the transesterification reaction yield. Catalysts mainly used can be classified attending to its chemical presence in the transesterification reaction: homogeneous or heterogeneous catalysts. Homogeneous catalysts act in the same liquid phase as the reaction mixture, whereas heterogeneous catalysts act in a different phase from the reaction mixture, usually as a solid. Currently, homogeneous catalysts applications due to their simple usage and less time required for oil conversion dominate the biodiesel industry. The widely used alkaline catalysts, NaOH and KOH, are easily soluble in methanol, forming sodium and potassium methoxide, respectively, catalytic species that lead the reaction to completion. The advantage of this process is the methyl esters production obtaining very high yields under mild conditions and that reaction generally takes short time for completion [7,13]. However, base catalyzed transesterification needs a high purity feedstock. Triglycerides and alcohol must be anhydrous in order to prevent undesirable saponification reactions (Fig. 3). Furthermore, triglycerides should have a strict low free fatty acids (FFA) proportion as these react with the alkaline catalyst and forms soaps (Fig. 4). The soap formation consumes the catalyst and decreases the ester yields. Moreover, the soap formed during the reaction prevents glycerol separation from biodiesel [14]. From a large scale industrial production point of view biodiesel manufacturing by homogeneously catalyzed transesterification reaction shows great disadvantages: production costs are high as the processes involve washing and purification steps in order to meet the stipulated biodiesel quality, it is quite difficult to remove K/Na traces remaining in the biodiesel product and glycerol separation process needs improvements. Besides, high amounts of water are needed in washing and consequent waste water treatment of the effluent adds to the overall process cost [15].

Homogeneous catalyzed transesterification downstream processing disadvantages have motivated intense research on heterogeneous catalyzed transesterification methods. In general, the heterogeneous catalyzed biodiesel production processes have less number of unit operations, with simple product separation and purification steps and no neutralization process is required [16]. The effectiveness of the heterogeneous catalytic conversion depends on the activity of the solid catalyst used. Three types of inorganic solid catalysts can be used to catalyze transesterification reaction: acidic character, basic character or bifunctional (acidic–basic character) solids.

In general, solid base catalysts are more active than solid acid catalysts requiring relatively shorter reaction times and lower reaction temperatures [17]. However, solid acid catalysts have several advantages over solid base catalysts such as the reaction is less affected by the presence of water and free fatty acids (FFA) [18]. The main advantage of solid acid catalysts is its ability to carry out the esterification of free fatty acids (Fig. 5), however the main advantage of solid base catalysts is its ability to carry out the transesterification of triglycerides. New trends are oriented toward the search for new solid catalysts that can simultaneously carry out esterification and transesterification reaction steps.

The present review discusses recent research related to several solid catalysts used in the esterification/transesterification reaction to produce biodiesel. Moreover, the main objective of this paper is to give an overview on the advancement of new solid catalysts for biodiesel production, performing simultaneously esterification and transesterification reaction. Besides, optimal reaction conditions exposed in bibliography for each bifunctional solid catalyst are presented.

2. Transesterification reaction by heterogeneous catalysts

Currently, transesterification reaction using basic catalysts is the most extended process to produce biodiesel. In this process it is necessary to use feedstocks (vegetable oils or animal fats) which present low free fatty acids content. When the raw materials contain high percentage of free fatty acids or water, the alkali catalyst reacts with the free fatty acids to forms soaps and the water can hydrolyze the triglycerides into diglycerides and form more free fatty acids [2].

Although in the last year some reviews about heterogeneous basic catalysts have been published [7,19], in this work only the latest effective catalysts for obtaining high FAME yields at low reaction temperatures will be discussed (Table 1).

Metal oxides are the basic heterogeneous catalysts group most studied. There are several metal oxides that have been studied in bibliography: calcium oxide, magnesium oxide, strontium oxide, mixed oxides and hydrotalcites.

CaO is the most widely used as a solid basic catalyst as it presents many advantages such as long catalyst life, high activity and requires only moderate reaction conditions [5]. Beside, CaO has attracted much attention due to the fact that there are several natural calcium sources from wastes, such as egg shells or mollusk shells. These shells are composed of calcium carbonates that are calcined in order to produce basic calcium oxide that can be used as a catalyst for the production of biodiesel [20,21]. Yoosuk et al. [22] have also used a calcite natural source to produce CaO. This natural source is cheap, it shows high basicity and it is environmental friendly. They demonstrated that hydration and subsequent thermal decomposition is an effective method to increase the activity of calcined natural calcite. This technique generates a calcium oxide with excellent textural properties and a large number of basic sites.

However, most researchers use neat CaO [23,24] or CaO from thermal decomposition of commercially available calcium salts such as calcium carbonate, calcium acetate, calcium oxalate and calcium nitrate [25–27]. All authors agree on obtaining good FAME yields using relatively low reaction temperatures, between 50 and 80 °C. However, the major inconvenience presented by the calcium oxide is that it requires a thermal activation in order to remove the adsorbed CO_2 and moisture. Then it is necessary to work under vacuum or nitrogen flow conditions in order to avoid its carbonation.

Table 1
Basic solids as catalysts for transesterification reaction.

Catalyst	Feedstock	Optimum reaction conditions	Biodiesel FAME yield	Refs.
CaO from waste shells of mollusk and egg	Palm olein oil	$T = 60\,^\circ C$, $t = 2$ h Methanol/oil = 18:1 Catalyst amount = 10 wt.%	>90%	[20]
CaO from eggshells	Palm oil	$T = 65\,^\circ C$, $t = 2$ h Methanol/oil = 12:1 Catalyst amount = 1.5 wt.%	98%[a]	[21]
CaO from natural calcites	Palm olein oil	$T = 60\,^\circ C$, $t = 45$ min Methanol/oil = 15:1 Catalyst amount = 7 wt.%	95.7%	[22]
CaO	Sunflower oil	$T = 80\,^\circ C$, $t = 5.5$ h Methanol/oil = 6:1 Catalyst amount = 1 wt.%	91%	[23]
CaO	Sunflower oil	$T = 75\,^\circ C$, $t = 45$ min Methanol/oil = 4:1 Catalyst amount = 1.2 wt.%	80%[a]	[24]
CaO (from $CaCO_3$)	Palm olein oil	$T = 60\,^\circ C$, $t = 1$ h Methanol/oil = 15:1 Catalyst amount = 7 wt.%	93.9%	[26]
KF/CaO	Chinese tallow seed oil	$T = 65\,^\circ C$, $t = 2.5$ h Methanol/oil = 12:1 Catalyst amount = 4 wt.%	96.8%	[28]
KNO_3/CaO	Rape oil	$T = 65\,^\circ C$, $t = 3$ h Methanol/oil = 6:1 Catalyst amount = 1 wt.%	98%[a]	[29]
CaO/ZnO	Ethyl butyrate	$T = 60\,^\circ C$, $t = 2$ h Methanol/oil = 12:1 Catalyst amount = 1.3 wt.%	>90%	[30]
CaO/Al_2O_3	Palm oil	$T = 64.29\,^\circ C$, $t = 5$ h Methanol/oil = 12.14:1 Catalyst amount = 5.97 wt.%	98.64%	[31]
CaO/Fe_3O_4	*Jatropha curcas* oil	$T = 70\,^\circ C$, $t = 80$ min Methanol/oil = 15:1 Catalyst amount = 2 wt.%	95%	[32]
Li/MgO	Soybean oil	$T = 60\,^\circ C$, $t = 2$ h Methanol/oil = 12:1 Catalyst amount = 9 wt.%	93.9%	[33]
KOH/MgO	Mutton fat	$T = 65\,^\circ C$, $t = 20$ min Methanol/oil = 22:1 Catalyst amount = 4 wt.%	>98%[a]	[34]
KI/Mg-Al mixed-metal oxides	Soybean oil	$T = 70\,^\circ C$, $t = 8$ h Methanol/oil = 20:1 Catalyst amount = 5 wt.%	>90%	[35]
Dolomite	Palm kernel oil	$T = 60\,^\circ C$, $t = 3$ h Methanol/oil = 30:1 Catalyst amount = 6 wt.%	98.0%	[37]
Dolomite	Canola oil	$T = 67.5\,^\circ C$, $t = 3$ h Methanol/oil = 6:1 Catalyst amount = 3 wt.%	91.78%	[38]
CaMgO and CaZnO	*Jatropha curcas* oil	$T = 65\,^\circ C$, $t = 6$ h Methanol/oil = 15:1 Catalyst amount = 4 wt.%	>80%[a]	[39]
KF/Ca-Al hydrotalcite	Palm oil	$T = 65\,^\circ C$, $t = 5$ h Methanol/oil = 12:1 Catalyst amount = 5 wt.%	97.98%	[40]
Mg-Al hydrotalcites commercial	Sunflower oil	$T = 60\,^\circ C$, $t = 24$ h Methanol/oil = 12:1 Catalyst amount = 2 wt.%	50%[a]	[42]
Mg-Al hydrotalcite	Soybean oil	$T = 230\,^\circ C$, $t = 1$ h Methanol/oil = 13:1 Catalyst amount = 5 wt.%	90%[a]	[43]
Mg-Al hydrotalcite	Jatropha oil	$T = 45\,^\circ C$, $t = 1.5$ h Methanol/oil = 4:1 Catalyst amount = 1 wt.%	95.2%	[44]
CaO/mesoporous silica	Soybean oil	$T = 60\,^\circ C$, $t = 8$ h Methanol/oil = 16:1 Catalyst amount = 5 wt.%	95.2%[a]	[45]
Sodium silicate	Soybean oil	$T = 60\,^\circ C$, $t = 1$ h Methanol/oil = 7.5:1 Catalyst amount = 3 wt.%	≈100%	[46]
Phosphazenium hydroxide/SiO_2	Soybean oil	$T = 75\,^\circ C$, $t = 12$ h Methanol/oil = 60:1 Catalyst amount ≈ 3.8 wt.%	≈90%[a]	[47]

[a] Presented by authors as “conversion” in bibliography.

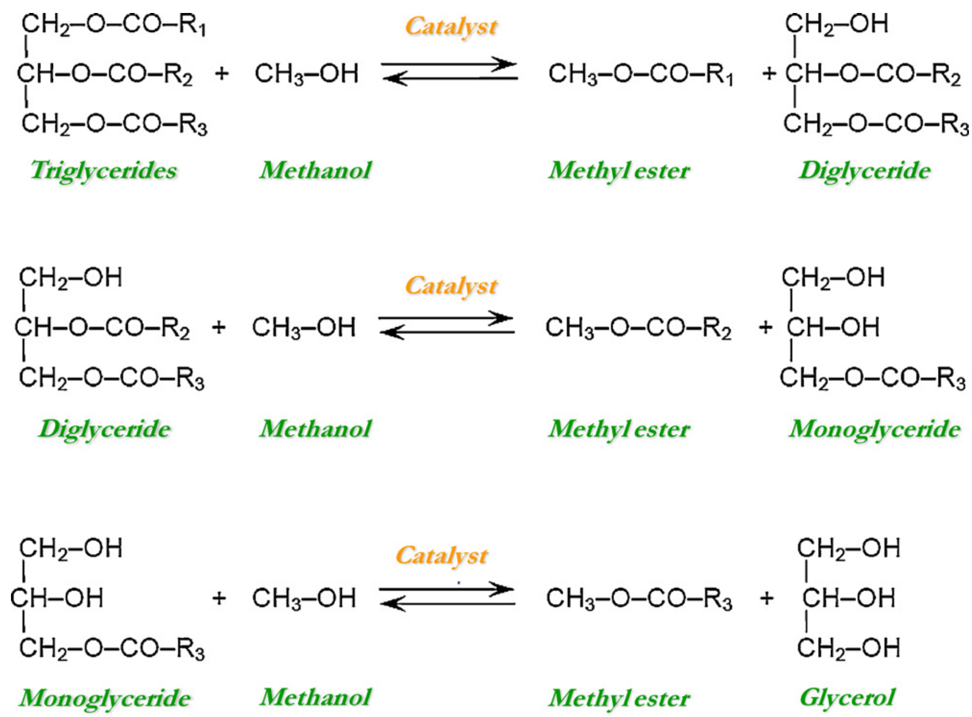


Fig. 2. Transesterification reaction steps.

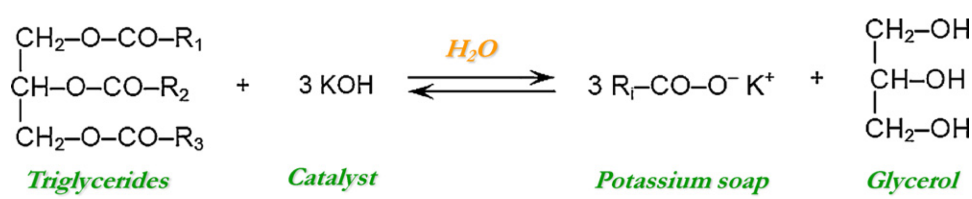


Fig. 3. Triglycerides saponification reaction.

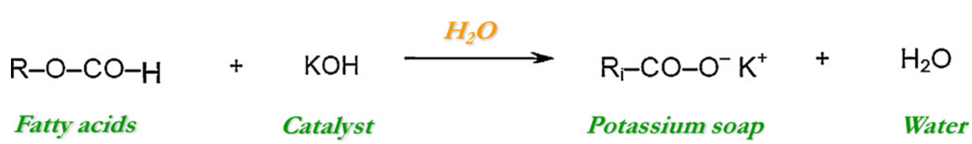


Fig. 4. FFA neutralization reaction.

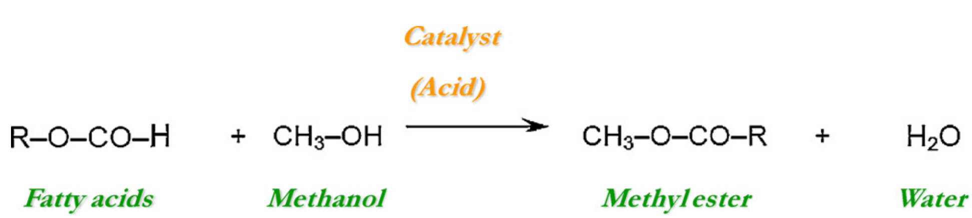


Fig. 5. Esterification reaction.

Adding a metallic element on its surface can increase the basic character shown by CaO. Wen et al. [28] prepared KF/CaO using impregnation method, obtaining 96% FAME yield for biodiesel production from Chinese tallow seed oil at 65 °C. Encimar et al. [29] developed CaO impregnated with KNO_3, reaching 98.5% FAME yield when the transesterification reaction was carried out at 65 °C using rape oil as feedstock.

CaO has been studied using it with other oxide compounds. Alba-Rubio et al. [30] studied CaO supported on zinc oxide as basic catalysts for transesterification processes. This supported CaO catalyst, thermally activated at 800 °C, can give rise to biodiesel yields higher than 90% after 2 h of reaction at 60 °C reaction temperature.

Zabeti et al. [31] studied the optimization of the methyl ester yield produced via transesterification of palm oil using CaO supported on alumina. The optimum reaction conditions obtained were approximately 12:1 alcohol/oil molar ratio, 6 wt.% catalyst amount, 5 h reaction time and 65 °C reaction temperature; under these conditions the FAME yield achieved was 98.64%. The

catalyst was reusable and the catalyst activity was sustained after two cycles.

Nanometer magnetic solid base catalysts were prepared by loading CaO on Fe_3O_4 [32]. The influence of the proportion of Ca^{2+} to Fe_3O_4 on the catalytic performance was studied. The catalyst with the highest activity was obtained when the proportion Ca^{2+} to Fe_3O_4 was 7:1; under the conditions of 15:1 methanol/oil molar ratio, 2 wt.% catalyst dosage and at 70 °C reaction temperature, the biodiesel yield reached was 95% in 80 min.

Magnesium oxide has also shown to possess catalytic activity for biodiesel synthesis. Magnesium oxide, produced by direct heating of magnesium carbonate or magnesium hydroxide, has the weakest basic strength and solubility in methanol among group II oxides [6]. In order to increase its basicity, MgO has been loaded with an active metal. Wen et al. [33] prepared a Li-doped MgO for biodiesel synthesis. The results showed that the formation of strong base sites is particularly promoted by the addition of Li, thus resulting in an FAME yield increase. The catalyst with 0.08 Li/Mg molar ratio calcined at 550 °C exhibits the highest FAME yield (93.9%) at 60 °C using 12:1 methanol/oil molar ratio and 9 wt.% catalyst amount. On the other hand, Mutreja et al. [34] prepared potassium hydroxide impregnated MgO as heterogeneous catalyst for the transesterification of mutton fat. Impregnation with 20 wt.% KOH increases the basic strength of MgO. Transesterification of mutton fat with 22:1 methanol/fat molar ratio at 65 °C resulted in a 98% conversion in 20 min.

Mixed-metal oxide systems can offer interesting properties, especially when each component differs remarkably from each other. For example, the combination of two oxides (alumina and magnesia) may establish new acid–base properties. The acid–base properties of alumina depend very much on the synthesis conditions and post-synthesis treatment. On the other hand, magnesia features a unique basic characteristic. Besides, the use of mixed-metal oxide as a support can introduce an interesting range of properties [35].

Fraile et al. [36] prepared several M(II)/M(III) mixed oxides where M(II) was Mg or Zn and M(III) was Al, Ga or La. These catalysts were tested in the sunflower oil transesterification reaction with methanol and methyl palmitate transesterification reaction with isobutanol. Results indicated that the strong basicity in mixed oxides was always connected to the presence of alkaline metals, independently of the M(II) and M(III) nature.

Tantirungrotechai et al. [35] synthesized via sol–gel a series of Mg-Al mixed-metal oxides with Mg/Al ratios in the range 0.125–8. These mixed oxides were also impregnated with KI in order to increase their base strength and their activities for soybean oil transesterification reaction with methanol. The KI impregnated Mg-Al mixed-metal oxide at 4:1 Mg/Al ratio was the most efficient catalyst for transesterification reaction at 70 °C reaction temperature (>90% conversion after 8 h).

Ngamcharussrivichai et al. [37] studied the transesterification reaction of palm kernel oil with methanol over dolomite. Dolomite, mainly consisting of $CaCO_3$ and $MgCO_3$, is a good heterogeneous base catalyst. The calcination of dolomite at 800 °C resulted in a Ca/Mg mixed oxide that presented activity for the methyl esters formation reaction at 60 °C reaction temperature. The reusability of calcined dolomite is minor than one showed for CaO. Ilgen [38] also conducted a study about the catalytic activity of dolomite. The heterogeneously catalyzed transesterification of canola oil was carried out using this mixed oxide as the catalyst to produce biodiesel. The FAME yield reached over 90% using calcinated (850 °C) dolomite when the reaction was carried out at methanol reflux temperature, with a 6:1 methanol/oil molar ratio, a 1.5 wt.% catalyst amount and 3 h reaction time.

Others calcium-based mixed oxides catalysts (CaMgO and CaZnO) have been investigated by Taufiq-Yap et al. [39] for the *Jatropha curcas* oil transesterification reaction from with methanol. Both CaMgO and CaZnO catalysts were prepared by coprecipitation method using the corresponding mixed metal nitrate solution in presence of a soluble carbonate salt. Their catalytic activities were compared with CaO. Both CaMgO and CaZnO catalysts showed high activity as CaO and they were easily separated from the product. Besides, CaMgO was found more active than CaZnO under the suitable transesterification conditions at 60 °C (4 wt.% catalyst amount, 15:1 methanol/oil molar ratio and 6 h reaction time), achieving a conversion higher than 80%. Using CaO as catalyst the reaction conversion decreased significantly after being reused for forth run, whereas using CaMgO and CaZnO as catalyst the conversion slightly decreased after sixth run.

Additionally, layered double hydroxide (LHDs) with general formula $[M_{(1-x)}{}^{2+}M_x{}^{3+}(OH)_2]^{x+}(A^{n-})_{x/n} \cdot yH_2O$, which is also called as hydrotalcite or hydrotalcite-like compound have shown to be suitable catalyst for the transesterification reaction. The hydrotalcite structure is based upon layered double hydroxides with brucite like ($Mg(OH)_2$) hydroxide layers containing octahedrally coordinated M^{2+} and M^{3+} cations. Hydrotalcites have been selected as catalyst of interest for transesterification reaction because of its strong surface basicity, high surface area and pore volume [40,41]. Navajas et al. [42] investigated a series of commercial Mg-Al hydrotalcites as catalyst for transesterification reaction concluding that their catalytic activity was modest compared with the results reported in the literature for hydrotalcites synthesized at the laboratory by coprecipitacion method. Moreover, Silva et al. [43] indicated that further investigations on experimental conditions optimization using hydrotalcite catalysts are still needed in order to improve the biodiesel production process due to high reaction temperatures are required. However, Deng et al. [44] obtained good FAME yields when hydrotalcite particles were used as heterogeneous catalyst in the transesterification reaction using an ultrasonic reactor. Gao et al. [40] also obtained high FAME yield using KF/Mg-Ca hydrotalcite as solid base catalyst in the palm oil transesterification reaction with methanol.

Moreover, the use of silica or silicates is taking great interest on the transesterification reaction for biodiesel production.

Calcium has been also supported on mesoporous silica. Samart et al. [45] studied the transesterification reaction of soybean oil with CaO/mesoporous silica. The optimized conditions found to be 15 wt.% Ca loading on the mesoporous silica, 5 wt.% catalyst amount and 60 °C reaction temperature for 8 h, providing a 95.2% FAME yield.

Guo et al. [46] examined the use of calcined sodium silicate as a solid base catalyst in the transesterification of soybean oil with methanol at 60 °C, achieving high activity with 4.0 wt.% water or 2.5 wt.% FFA contained in soybean oil. However, a considerable loss in catalytic activity was observed when the catalyst was recycled for more than five times. Hence, as sodium silicate is a low-cost solid base catalyst, it can also be used in the transesterification of crude oil containing amounts of water and FFA.

Kim et al. [47], investigated the catalytic activity of a phosphazenium hydroxide incorporated onto silica as catalyst for vegetable oils transesterification with methanol in a 55–75 °C reaction temperature range. The catalyst exhibited high activity due to its strong basicity, achieving approximately 90% conversion at 75 °C.

The major drawback of the catalysts discussed is its unsuitability toward very high FFA content feedstocks and soaps can be produced. In this regard, the oil feedstock would need to be pre-treated in order to reduce its high FFA content. Other alternative could be the usage of a two-step catalytic process (a first step in which FFA were converted by the use of an acid catalyst and a second step in which a base catalyst was used to convert triglycerides to FAME) or the use of bifunctional catalysts (those that catalyze both free

fatty acids esterification reaction and triglycerides transesterification reaction at the same time).

3. Esterification reaction by heterogeneous catalysts

The cost of raw materials (mainly triglycerides) in biodiesel industry represents the main production cost. However, it is possible to use low cost feedstocks, like non-edible oils, fried waste oils and animal fats which could be converted to biodiesel, thus decreasing production costs and performing a more environmental friendly biodiesel production process. The main problem of processing low cost feedstock lies in their large amount of free fatty acids that cannot be converted into biodiesel using a basic catalyst. Free fatty acids can react with the basic catalyst (neutralization reaction), accelerating the basic catalyst deactivation. Consequently, FFA contained in used vegetable oil should be previously removed or converted to FAME join to biodiesel production process [48,49].

A previous free fatty acids esterification reaction is an alternative process to transesterification reaction when low-quality oils and fats are used as feedstocks. Esterification is normally carried out in a homogeneous phase in the presence of acid catalysts such as H_2SO_4, HF, H_3PO_4, HCl and p-toluene sulfonic acid [50,51]. However, the use of these catalysts is dangerous because they are hazardous and corrosive liquid acids. Therefore, acid heterogeneous catalysts can be considered as an alternative to minimize environmental damage and reduce biodiesel cost [52].

The following section will give an overview of the recent research related to acid heterogeneous catalysts studied in the esterification reaction to produce biodiesel.

Several acid solids have been tested in the FFA esterification reaction, such as: zirconium oxide, titanium oxide, tin oxide, sulfonic ion-exchange resin, sulfonic modified mesostructure silica, sulfonated carbon-based catalyst, heteropolyacids (HPAs) [12]; however in the last year the use of aluminosilicates (mordenita, halloysite, kaolinite), zirconium oxides and cation-exchange resins as heterogeneous acid solids is an important issue.

SathyaSelvabala et al. [53] demonstrated that H-Mordenite (Al/Si ratio = 19) treated with phosphoric acid is an efficient alternative to homogeneous acid catalyst for esterification of FFA in neem oil. During phosphoric acid modification hydrophobic character and weak acid sites of the mordenite were increased, which lead to better esterification when compared to H-mordenite. The esterification process analyzed in that study showed that the amount of FFA was reduced from 24.4 to 1.8 mg KOH/g oil. The optimum reaction parameters were found to be: 6:1 methanol/oil molar ratio; 1% catalyst loading and 60 °C reaction temperature.

Zatta et al. [54] investigated the methylic and ethylic esterification of lauric acid using raw halloysite as heterogeneous catalyst. The reactions were conducted at several alcohol:lauric acid molar ratios and catalyst proportions, at 160 °C for 2 h in a pressurized steel reactor. Halloysite produced a lauric acid conversion of 95.02% and 87.11% for the methylic and ethylic esterifications, respectively. The results showed that halloysite is a promising inexpensive and reusable material for esterification reactions involving fatty acids.

Nascimento et al. [52] prepared catalysts for esterification of oleic acid with methanol from two Amazon kaolins (Century and flint) and two standard kaolins. Sample of kaolinites were thermally treated at 950 °C, providing metakaolins samples, and leached with 4 M sulfuric acid solutions. The acidity evaluation of the acid-activated metakaolins confirmed the presence of both Brönsted and Lewis acid sites, with Century metakaolin presenting the highest values. All of the metakaolins studied showed catalytic activity for the esterification of oleic acid with methanol. The analysis of conversion values obtained revealed a correlation with Al content and acidity for each prepared sample. From these results, kaolin could be considered a promising material for the production of catalysts for the esterification of oleic acid with methanol.

However, the usage of zirconium oxides as a solid acid for esterification reaction is the most extended. This support is the most used for esterification reaction due to its high number of Brönsted acid sites. The number of Brönsted acid sites is an important criterion for selection of an efficient support [55].

Tungsten oxide zirconia was examined as catalyst for used vegetable oils conversion to fatty acid methyl esters achieving high activity and no leaching [49,56]. Among the WO_3/ZrO_2 catalysts with several WO_3 loading amount from 10 to 30 wt.%, 20 wt.% WO_3/ZrO_2 showed the highest catalytic activity. The strong acidity of this catalyst is one of the reasons for its high catalytic activity.

Kim et al. [57], have developed a class of zirconia supported metaloxide catalysts in order to use brown grease (acid value: 178 mg KOH/g) for obtaining biodiesel. High FAME yields through esterification of FFA were achieved. In particular, a ZnO/ZrO_2 catalyst showed a high FAME yield and displayed high durability. The total acid number measured for the product converted over ZnO/ZrO_2, was 12 mg KOH/g, representing a FAME yield of 78%.

Rattanaphra et al. [58] studied myristic acid esterification with methanol in presence of triglycerides using sulfated zirconia as heterogeneous catalyst. It could be seen that when the concentration of myristic acid methyl ester was increased, a dramatic decrease in the FFA concentration during the first 20 min was observed. Sulfated zirconia can be classified as a heterogeneous superacid catalyst. It has recently received considerable attention as a promising catalyst for industrial processes due to its strong acid properties. It also shows higher acid strength than heteropolyacid, suflonic ion-exchange resins and other heterogeneous acid catalysts [59,60], however, the leaching of sulfate groups was observed when the catalyst was used several times.

Although ZrO_2 has showed a good performance as support for esterification reaction using low cost feedstocks that often contained high levels of free fatty acids, its cost is prohibitively high for use in biodiesel production, as zirconium is a rare and costly metal. Therefore, it will be necessary to find a cheaper and available support which present strong acidity.

Furthermore, cation-exchange resins as solid acids can be used as heterogeneous catalyst for esterification reaction. Their catalytic activity strongly depends on their swelling properties because the swelling capacity controls reactants accessibility to the acid sites and, therefore, affects their overall reactivity [18]. Additionally, cation-exchange resins can offer better selectivity toward the desired products and better reusability compared to homogeneous acid catalysts. Feng et al. [61] used three cation-exchange resins in order to examine their activity on the esterification reaction of acidified oil. The highest FFA conversion obtained was approximately 90% using a resin that showed excellent reusability. This cation-exchange resin was used as solid acid catalyst in a fixed bed reactor to carry out the continuous esterification reaction of acidified oil with methanol [62]. High FFA conversion and operational stability was observed and the loss of sulfonic acid groups from the cation-exchange resin during continuous esterification was not found. The use of Amberlysts, acid ion-exchange resins, has also been widely studied on esterification reaction to produce biodiesel [63–66].

In general, as can be found in bibliography, high reaction temperatures are needed to carry out the FFA esterification to FAME (Table 2); as an alternative procedure, the use of heterogeneous catalysts for both transesterification and esterification reaction is being increasingly studied with the possibility of using at lower temperatures than those used in the esterification reaction.

Table 2
Acids solids as catalysts for esterification reaction.

Catalyst	Feedstock	Reaction temperature	Refs.
Kaolins	Oleic acid	160 °C	[52]
Raw halloysite	Lauric acid	160 °C	[54]
WO_3/ZrO_2	Waste acid oil	150 °C	[56]
ZnO/ZrO_2	Brown grease	200 °C	[57]
SO_4^{2-}/ZrO_2	Rapeseed oil + miristic acid	120–170 °C	[58]
Ionic exchange resin	Soybean oil + oleic acid	100 °C	[63]
Amberlyst	Soybean oil + oleic acid	80 °C	[64]
Amberlyst	Cooking sunflower oil + acid oleic	100 °C	[66]

4. Simultaneous esterification and transesterification reaction by heterogeneous catalysts

Due to high FFA content in low cost feedstocks, the alkali catalyzed transesterification reaction to produce biodiesel gives low biodiesel yield because FFA reacts with alkali to form soap, resulting in serious emulsification and separation problems. To solve this problem, production of biodiesel by a two-step catalytic process has been recently developed. In a first step, a feedstock pretreatment is performed in which the free fatty acid content is reduced by the use of an acid catalyst such as sulfuric acid or ferric sulfate and in a second step a basic catalyst is used to produce biodiesel [67–69]. Wang et al. [70] and Patil et al. [71] carried out a two-step FAME production process in order to convert waste cooking oil to methyl esters. The process involved the esterification reaction (FFA conversion to FAME) using ferric sulfate following by transesterification (triglycerides conversion to FAME) using KOH.

However, the two-step method also faces the problem of catalyst removal in both steps. The catalyst removal problem in the first step can be avoided by neutralizing the acid catalyst, using extra alkaline catalyst in the second step. However, the use of extra catalyst will increase the cost of biodiesel production. Generally, the residue of either alkaline or acidic catalyst in the biodiesel product can cause engine problems. Alkaline catalyst can produce higher levels of incombustible ash and acid catalyst attacks engine metallic parts. Therefore, both catalysts must always be eliminated from the biodiesel when the reaction is completed [1,72].

In order to avoid these problems and due to the fact that the main advantage of solid acid catalysts is its ability for free fatty acids esterification and the main advantage of solid basic catalysts is its ability to carry out the transesterification of triglycerides, it would be suitable to find a solid catalyst which acts as an acid and a base at the same time. The bifunctional solid catalysts are presented as an alternative to the biodiesel production in order to develop simultaneously the esterification and transesterification reaction. The new bifunctional heterogeneous catalysts developed in the last year are studied below.

Kondamudi et al. [14] tested the catalytic activity of Quintinite-3T as bifunctional heterogeneous catalyst that converts FFA and triglycerides simultaneously into biodiesel. The catalyst was prepared by sol–gel process and tested for soy, canola, coffee and waste vegetable oils with variable amounts of FFA (0–30 wt.%). The catalyst successfully converted both FFA and triglycerides a single step batch reactor.

Salinas et al. [73] studied potassium supported on titania as catalyst for the production of biodiesel from canola oil. It was found that low loadings of potassium lead to the formation of weak basic sites on the acid support (titania). This catalyst presented interesting activities and it showed a robust character since no need for in situ pre-treatment or inert reaction environment were needed.

Wen et al. [74] prepared MgO/TiO_2 mixed oxide catalysts by the sol–gel method and these catalysts were successfully used for biodiesel production. The addition of Ti resulted in the substitution of Ti ions for Mg ions in the magnesia lattice, thus leading to defects on the catalyst surface. These defects can improve the stability while maintaining an acceptable catalytic activity in the transesterification reaction for the biodiesel production. The best catalyst was determined to be 1 Mg/Ti molar ratio calcined at 923 K, based on an assessment of the activity and stability of the catalyst. Its catalytic activity decreased slowly within the reuse processes. However, after regeneration, its activity was slightly increased compared with the fresh catalyst activity due to an increase in the specific surface area and average pore diameter. This mixed oxides catalyst, MgO/TiO_2, showed high potential in large-scale biodiesel production from waste cooking oil.

Macario et al. [75] studied the transesterification of triglycerides contained in waste oilseed fruits with methanol in heterogeneous/homogeneous systems using acid and basic catalysts. The acid catalysts (strong acid catalysts: USY, BEA, FAU-X, and weak acid catalysts: MCM-41 and ITQ-6) were prepared by hydrothermal synthesis procedures. In order to obtain acid–base catalysts, potassium was loaded on different materials by ionic exchange (obtaining K-MCM-41 and K-ITQ-6). K-ITQ-6 catalysts achieved the highest triglycerides conversion and biodiesel yield values, after 24 h of reaction at 180 °C. Modification of ITQ-6 surface with K^+ ions produced a catalyst with weak Brønsted acid sites and basic sites, responsible of its catalytic activity in triglycerides transesterification and FFA esterification. The catalyst is active toward the conversion of waste oil with high free fatty acid contents (5.58%) without formation of undesired by-product (soap-compounds) and it promotes a simultaneous homogeneous/heterogeneous and acid/base catalysis. Deactivation of this catalyst occurs due to potassium leaching, but its regeneration and reuse are feasible and easy to perform.

Cannilla et al. [76] reported the use of a novel MnCeOx system in the refined sunflower oil transesterification reaction with methanol. A series of manganese-ceria catalysts, with Mn/Ce atomic ratio ranging between 0.4 and 3.4, was prepared via the redox-precipitation route. Independently of Mn loading, the redox-precipitation method for the preparation of Mn-based systems allowed to obtain always high dispersed catalysts and, as a consequence, a linear relationship between reaction rate and Mn loading was obtained. NH_3-TPD and CO_2-TPD measurements indicate that MnCeOx systems are characterized by a prevalent nature of basic sites. However, the catalyst performance is the result of a synergic role played by both the surface acid/base character and textural porosity.Jiménez-López et al. [77] prepared a series of zirconium doped MCM-41 silica supported WO_x solid acid catalysts by impregnation with ammonium metatungstate, with WO_3 loading ranging from 5 to 25 wt.%. The maximum activity (82 wt.% of FAME yield) was found for the catalyst with 15 wt.% WO_3 loading, which was able to simultaneously catalyze the esterification reaction of FFA and transesterification of triglycerides present in a simulated used oil, with high acidity degree (9.1%). Moreover, the catalytic activity was maintained in the presence of 5 wt.% of water and after three cycles of reutilization, without any catalyst treatment.

Omar and Amin [78] carried out the heterogeneous transesterification of waste cooking palm oil to biodiesel over Sr/ZrO_2 catalyst.

Table 3
Bifunctional heterogeneous catalysts for simultaneous esterification and transesterification reactions.

Catalyst	Feedstock	FFA (wt.%)	Optimum reaction conditions	Biodiesel FAME yield	Refs.
Quintinite-3T	Canola oil	–	T = 75 °C, t = 2 h Methanol/oil = 12:1 Catalyst amount = 10 wt.%	97.28%[b]	[14]
	Waste vegetable oil	15	T = 75 °C, t = 6 h Methanol/oil = 12:1 Catalyst amount = 10 wt.%	97.72%[b]	
	Coffee oil	33	T = 75 °C, t = 4 h Methanol/oil = 12:1 Catalyst amount = 10 wt.%	96.6%[b]	
K/TiO_2	Canola oil	–	T = 70 °C, t = 5 h Methanol/oil = 36:1 Catalyst amount = 6 wt.%	100%[b]	[73]
MgO/TiO_2	Waste cooking oil	3.6[a]	T = 170 °C, t = 6 h Methanol/oil = 50:1 Catalyst amount = 10 wt.%	91.6%	[74]
K-ITQ-6	Waste oilseed fruits	5.58	T = 180 °C, t = 48 h Methanol/oil = 20:1 Catalyst amount = 5 wt.%	87%	[75]
$MnCeO_x$	Sunflower oil	0.07	T = 140 °C, t = 5 h Methanol/oil = 12:1 Catalyst amount = 1 wt.%	≈86%	[76]
WO_3/Zr-MCM-41	Sunflower oil	9.1	T = 115.5 °C, t = 2.5 h Methanol/oil = 12:1 Catalyst amount = 10 wt.%	79.7%	[77]
Sr/ZrO_2	Waste cooking palm oil	5.08[a]	T = 115.5 °C, t = 87 min Methanol/oil = 29:1 Catalyst amount = 2.7 wt.%	FAME yield = 79.7%	[78]
K-Pumice	Sunflower oil	0.17[a]	T = 55 °C, t = 2 h Methanol/oil = 18:1 Catalyst amount = 20 wt.%	95.6%	[79]
	Waste oil	2.02[a]	T = 60 °C, t = 4 h Methanol/oil = 21:1 Catalyst amount = 20 wt.%	90.9%	

[a] Acid value (mg KOH/g).
[b] Presented by authors as "conversion" in bibliography.

Table 4
Strong acids solids as catalysts for simultaneous esterification and transesterification reactions.

Catalyst	Feedstock	FFA (wt.%)	Optimum reaction conditions	Biodiesel FAME yield	Refs.
SO_4-ZrO_2	Purified palm oil	–	T = 250 °C, t = 10 min Methanol/oil = 25:1 Catalyst amount = 0.5 wt.%	90%[b]	[81]
	Palm fatty acids	93	T = 250 °C, t = 1 min Methanol/oil = 6:1 Catalyst amount = 0.5 wt.%	75%[b]	
$SO_4^{2-}/ZrO_2/Al_2O_3$	*Jatropha curcas* L. oil	0.0227[a]	T = 150 °C, t = 4 h Methanol/oil = 9.88:1 Catalyst amount = 7.61 wt.%	90.32%	[83]
$SO_4^{2-}/ZrO_2/SiO_2$	Sunflower oil	9	T = 200 °C, t = 6 h Ethanol/oil = 12:1 Catalyst amount = 14.6 wt.%	91.5%	[84]
SO_4^{2-}/ZrO_2-TiO_2/La^{3+}	Acid oil	119.58[a]	T = 200 °C, t = 2 h Methanol/oil = 15:1 Catalyst amount = 5 wt.%	90%	[85]
Fe-Zn cyanide complexes	Vegetable oil	10	T = 160 °C, t = 8 h Methanol/oil = 16:1 Catalyst amount = 3 wt.%	98%[b]	[86]
Carbon-based solid acid	Cottonseed oil	50	T = 220 °C, t = 4.5 h Methanol/oil = 16.8:1 Catalyst amount = 0.2 wt.%	94.8%[b]	[87]
SO_4^{2-}/SnO_2-SiO_2	*Croton megalocorpus* oil	4.8[a]	T = 180 °C, t = 2 h Methanol/oil = 15:1 Catalyst amount = 3 wt.%	95%	[88]
	Moringa oleifera oil	2.2[a]	T = 150 °C, t = 2.5 h Methanol/oil = 19.5:1 Catalyst amount = 3 wt.%	84%	[89]

[a] Acid value (mg KOH/g).
[b] Presented by authors as "conversion" in bibliography.

Strontium metal doped on catalyst increased the amphoteric nature of zirconia, which contained basic and acid sites. The presence of both basic and acid sites in Sr/ZrO_2 facilitated simultaneous transesterification and esterification reactions.

Borges et al. [79] have studied natural porous silica material, pumice, as heterogeneous catalyst in the transesterification reaction of sunflower oil and waste oil with methanol for biodiesel production. This low cost natural porous material was subjected to ion exchange with a KOH aqueous solution in order to increase its activity. Potassium was loaded in the pumice natural material by ionic exchange. It demonstrated to be an efficient heterogeneous particulate catalyst for the triglycerides transesterification and free fatty acids esterification from sunflower oil and waste oil at low temperature (55 °C). The high yields obtained with waste oil as feedstock indicated a bifunctional behavior of the catalytic material.

The optimum reaction conditions for bifunctional solid catalysts summarized in this work are showed in Table 3.

Other way to biodiesel production from both FFA esterification and triglycerides transesterification is the use of strong acids solids with a high concentration of catalytic sites [80]. Then, an overview about the latest strong solid acids developed is showed.

Petchmala et al. [81] demonstrated that FAME production by transesterification of purified palm oil and esterification of palm fatty acids in near-critical and super-critical methanol was efficient in the presence of SO_4-ZrO_2 catalyst. Sulfated zirconia catalysts were prepared with several sulfur loading contents and two calcination temperatures (500 °C, 700 °C). The NH_3 and CO_2 TPD measures revealed that the sulfur content and calcination temperature strongly affects the catalyst base–acid site and thus the catalytic reactivity. The amount of acid sites increased with sulfur content in ZrO_2 until 1.8% value, and it decreased with further sulfur loading (2.5%). The abundance of base sites decreased proportionately with the sulfur content in ZrO_2. In addition, when calcination temperature increased, the amount of acid sites decreased while the base sites increased. SO_4-ZrO_2 with 1.8% sulfur loading content calcined at 500 °C proved to be the most active catalyst for the palm oil transesterification and the palm fatty acids esterification reactions.

Due to the fact that sulfated zirconia is a heterogeneous acid catalyst with very strong acidic sites [82], in the last year some researchers have supported it on alumina [83] and silica [84], getting esterification and transesterification simultaneous reactions for vegetable oils with high FFA content as feedstock, using appropriate operation conditions.

Moreover, Li et al. [85] prepared a new type of superacid solid catalyst (SO_4^{2-}/ZrO_2-TiO_2) loaded with lanthanum, which was prepared by precipitation and impregnation method. This superacid solid catalyst proved to be effective for simultaneous transesterification and esterification reactions using acid oil containing about 60 wt.% free fatty acids as feedstock. The catalyst was reutilized for five runs showing little loss in activity.

Yan et al. [86] reported double-metal cyanide complexes of Fe^{2+} and Zn^{2+} as solid catalyst for biodiesel production from vegetable oils by combined esterification/transesterification reactions. This catalyst was prepared through co-reaction of potassium ferrocyanide, zinc chloride and complexing agent of tert-butanol. It was demonstrated that the catalyst preparation method significantly influences its physical (surface area and crystallinity) and catalytic properties. The surfactant molecules might have an effect on reducing the crystanillity and increasing the density of actives sites, thereby increasing the catalytic activity in both esterification and transesterification reactions. It was found that unsaturated Zn^{2+} is probably the active (Lewis acid) site for both esterification and transesterification reactions.

Shu et al. [87] prepared a carbon-based solid acid catalyst by sulfonation of carbonized vegetable oil asphalt. This catalyst was employed to simultaneously catalyze esterification and transesterification reaction to synthesize biodiesel when a waste vegetable oil with large amounts of free fatty acids was used as feedstock. The solid acid consisted of a flexible carbon-based framework with highly dispersed polycyclic aromatic hydrocarbons containing sulfonic acid groups. The high catalytic activity and stability of this catalyst was related to its high acid site density (—OH, Brönsted acid sites), hydrophobicity that prevented the hydration of —OH species, hydrophilic functional groups (—SO_3H) that gave improved accessibility of methanol to the triglyceride and FFAs, and large pores that provided more acid sites for the reactants.

Some researchers have successfully produced biodiesel from *Croton megalocorpus* oil [88] and *Moringa oleifera* oil [89] using sulfated tin oxide enhanced with SiO_2 (SO_4^{2-}/SnO_2-SiO_2) as super acid solid catalyst. The catalyst was found to be able to perform esterification and transesterification reactions simultaneously in which the acid value in the oils was reduced to a minimum value and high yield of biodiesel could be attained without producing any soap.

The optimum reaction conditions for each strong acid solid discussed before are showed in Table 4.

5. Future perspectives

The presence of acid and basic sites on the surface of a catalyst shows to be the best future development to produce biodiesel using heterogeneous catalysis as it avoids the problems caused by the use of homogeneous catalysts and, moreover, it allows carrying out the biodiesel production process in a single step.

The bifunctional solids and the strong acids solids as catalysts are presented as the new way to develop the biodiesel production by heterogeneous catalytic transesterification reaction, because they can catalyzed both free fatty acids esterification reaction and triglycerides transesterification at the same time.

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